



The catalytic activity of Pd/WO_x/γ-Al₂O₃ for hydrodeoxygenation of guaiacol



Yoon-Ki Hong^a, Dae-Won Lee^{a,*}, Hee-Jun Eom^a, Kwan-Young Lee^{a,b,**}

^a Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea

^b Green School, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea

ARTICLE INFO

Article history:

Received 11 July 2013

Received in revised form

19 December 2013

Accepted 24 December 2013

Available online 3 January 2014

Keywords:

Hydrodeoxygenation (HDO)

Guaiacol (2-methoxyphenol)

Palladium

Tungsten oxide

Metal-support interaction

ABSTRACT

In this study, Pd/WO_x/γ-Al₂O₃ was examined as a catalyst for the catalytic hydrodeoxygenation (HDO) of guaiacol (2-methoxyphenol), which is a model molecule for the bio-oils derived from lignocellulose biomass. The HDO activity of the catalyst was governed by its surface acidity and the physicochemical state of palladium. The surface acidity of the catalyst was closely related to the surface density of tungstate on the alumina support. The density of the tungstate was the highest (3.7–5.0 W/nm²) when it was mono-layered. The highest HDO activity was obtained with Pd32WA (Pd/WO_x/γ-Al₂O₃ containing 2 wt.% Pd and 32 wt.% W) in which the tungstate formed a near-perfect monolayer on the support and the amount of surface acidity reached the highest. Palladium interacted closely with the tungstate, making the tungsten relatively electron-rich (less electron-deficient) due to the electron transfer from Pd to W. The interaction also caused the perimeter of the palladium particle to become partially decorated with a tungstate overlayer. The palladium species on WO_x/Al₂O₃ was more HDO-active than the palladium species supported on other acidic supports (SiO₂/Al₂O₃) similar to WO_x/Al₂O₃ in surface acidity. The results indicated that the catalysis progressed through a bi-functional mechanism in which the aromatic ring of guaiacol was fully hydrogenated by a Pd species to form 2-methoxycyclohexanol, which was subsequently deoxygenated by the acidic sites on the Pd–WO_x surface to generate cyclohexane. When using Pd32WA, we could achieve a 100% guaiacol conversion and an 88% yield of cyclohexane (C₁-based) under the given reaction conditions.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

As the resources of conventional petroleum crude dwindle, there are increased needs for using unconventional but alternative petroleum resources such as shale oils, oils sands, extra heavy oils, bio-fuels. Before use, such unconventional resources should be chemically processed or upgraded. For example, heavy oil is deficient in hydrogen and high content of sulfur and metallic impurities [1]. It is necessary to lower its viscosity and remove the impurities through the hydrotreating processes such as hydrocracking, hydrodesulfurization (HDS), hydrodemetallation (HDM), etc. Another promising example of unconventional resources is bio-fuel (bio-oil). Bio-oils, obtained from raw biomass through thermochemical processes [2–4], have a low LHV (40–45% of the

LHV (weight basis) of commercial petroleum oils), a high viscosity and innate chemical instability due to a high concentration of oxygen (up to 50 wt.%) [5–7]. Bio-oils need *hydrodeoxygenation* (HDO) process to eliminate the oxygen, either totally or partially, and generate a material more suited for use. We focused on the HDO and achieved this end using heterogeneous catalytic system.

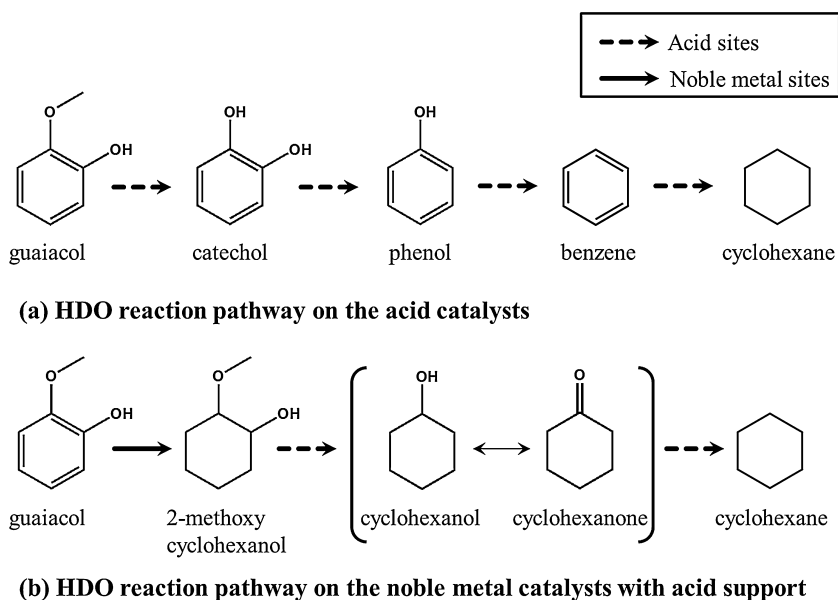
We selected guaiacol (2-methoxyphenol) as a model reactant (or probe molecule representing the bio-oil) for the HDO reaction. Guaiacol is an adequate model molecule to investigate the catalysis on HDO because it has two functional groups which contain oxygen (hydroxyl and methoxy groups). Therefore, because many other researchers have utilized guaiacol in their studies about HDO reactions [5,6,8–17], we also selected guaiacol as a model reactant molecule.

The catalysts used in catalytic HDO reactions can be divided into two groups: the sulfided catalysts [5,9–14,18–21] and the noble metal catalysts [6,22–24]. Delmon's group had studied the HDO of guaiacol over sulfided molybdenum catalysts (supported NiMo and CoMo) extensively during the mid-nineties [5,9–14]. The sulfided molybdenum catalysts are well known for their commercial applications in HDS reactions. For the sulfided Mo catalysts, the reaction characteristics of HDO were similar to those of HDS. On the

* Corresponding author. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.

** Corresponding author at: Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.

E-mail addresses: stayheavy@korea.ac.kr (D.-W. Lee), kylee@korea.ac.kr (K.-Y. Lee).



Scheme 1. Pathways for the HDO reaction of guaiacol using an acid catalyst and a bifunctional catalyst (noble metal and acid catalyst) [22].

sulfided catalysts, guaiacol was hydrodeoxygenated via demethylation, demethoxylation and dehydroxylation. The Lewis acidic sites, which develop mostly on alumina surface, are primarily responsible for the cleavage of O-methyl bond (i.e., demethylation). The demethylation also takes place preferentially on the sulfided phase, involving a proton (H^+) and a hydride anion (H^-). The proton reacts with the partially negative oxygen atom (δ^-), while the hydride anion adds to the partially positive carbon atom in methoxy group ($-OC^{\delta+}H_3$) [11]. However, when applying the sulfide catalysts to HDO reaction, sulfur leaches from the catalyst and causes serious problems: it not only deactivates the catalyst but also contaminates the reaction products [6,25], making the use of sulfided catalysts challenging.

Another group of catalysts used for the HDO of guaiacol is noble metal catalysts [6,22–24]. In this group of catalysts, a high HDO activity could be obtained when noble metals, such as Pd, Rh, Pt and Ru, were paired with an acidic support, such as γ - Al_2O_3 , SiO_2 - Al_2O_3 , acid-treated carbon and others [22]. Lee et al. suggested that the reaction pathway of HDO over the noble metal-supported acidic oxide catalysts occurred as described in Scheme 1 [22]. The catalytic process progressed through a *step-wise, bi-functional* mechanism (Scheme 1(b)): (1) the ring hydrogenation (de-aromatization) of guaiacol into 2-methoxycyclohexanol on the noble metal site; (2) the deoxygenation of 2-methoxy cyclohexanol and its products (demethoxylation, dehydroxylation) on the metal-deposited acid site.

The supported tungsten oxide (WO_x) is a versatile solid acid catalyst used to catalyze various heterogeneous reactions, such as the isomerization of alkenes [26] and alkanes [27], selective catalytic reduction of NO_x with NH_3 [28,29], olefin metathesis, hydrocarbon cracking and most notably, HDS of dibenzothiophenes [30,31] and diesel fuels [32]. Both Lewis and Brønsted acidic sites are present on WO_x/Al_2O_3 in distributions dependent upon the loading of the tungsten oxide (WO_x) [33–36]. According to other studies, the crystallographic phase of the WO_x species changes along with its surface coverage [37–40]. At low W surface coverage (<2 W atoms/ nm^2), the monotungstate species are dominant. These species change to a polytungstate bulk phase as the surface W coverage increases to intermediate values (3–5 W atoms/ nm^2). As the W coverage increases higher (>5 W atoms/ nm^2), the crystalline WO_3 particulates form on top of the polytungstate layer.

Among the noble metals, palladium has been most widely used as the active metal in selective hydrogenation catalysts [41–45]. In many cases, the electronic and morphological properties of palladium species are influenced by interaction with the support material; both of these properties strongly affect the hydrogenation activity of the catalysts [41–45]. The metal–support interaction also influences the thermal diffusion rate of the metal species, which is directly related to the thermal durability of the catalysts. Several papers have discussed the interactions between the palladium and tungsten oxide in Pd/ WO_x supported catalysts [46–49]; it was reported that the degree of the Pd- WO_x interaction critically influenced the catalytic activity in hydrogenation reactions, such as the partial hydrogenation of hept-1-yne [48] or the selective hydrogenation of styrene [49]. The Pd/ WO_x is a sort of noble metal-acidic support pair but, in spite of the reports of its good performance in other hydrogenation reactions, there has not been a study detailing its application to the HDO of guaiacol or other bio-oil-related model compounds.

In this study, we examined the activity of Pd/ WO_x/Al_2O_3 catalysts for HDO of guaiacol. In particular, we investigated the influences of the acidic properties of the WO_x layer, as well as the Pd- WO_x interaction, on the HDO activity of the Pd/ WO_x/Al_2O_3 catalysts. The results strongly suggested that the catalysis occurs through a *bi-functional* HDO mechanism.

2. Experimental

2.1. Preparation of catalysts

Tungsten oxide was impregnated on γ - Al_2O_3 (Sasol, Disperal P2, $V_p = 0.48$ cm³/g, $S_a = 264$ m² g⁻¹) with an incipient-wetness method using aqueous solutions of ammonium metatungstate hydrate (Aldrich, 72.4% W). The sample was dried at 110 °C overnight and calcined at 500 °C for 15 h under an atmosphere of air. The impregnated materials (WO_x/Al_2O_3) were named $\circ\circ$ WA, which indicates that $\circ\circ$ wt.% of W was loaded onto the Al_2O_3 supports. To compare WA with different acidic support materials, SiO_2 - Al_2O_3 supports with different Si/Al ratios were prepared using a previously reported sol-gel method [50]. The prepared SiO_2 - Al_2O_3 supports were named SA-X, which X means the atomic molar ratio of Si to Al.

Table 1
Chemical composition, specific surface area and surface W density of the PdWA catalysts.

Nomenclature	Pd concentration ^a (wt.% Pd)	W concentration ^a (wt.% W)	Specific surface area ^b (SSA, m ² g ⁻¹)	Surface density ^c (SD, W/nm ²)
PdAl	2.1	0	238.6	0
Pd9WA	2.1	9.2	219.5	1.3
Pd14WA	2.0	14.0	199.3	2.0
Pd19WA	2.0	19.1	190.5	2.8
Pd26WA	2.0	26.3	184.2	3.7
Pd32WA	2.0	31.6	157.3	5.0
Pd38WA	2.0	37.8	139.9	6.4
Pd53WA	2.0	52.5	118.8	9.5

^a Estimated from the Pd and W content obtained by ICP-AES.

^b BET surface areas of the supports were analyzed by N₂ adsorption using ASAP2010.

^c Calculated from Eq. (1).

On the support materials, 2 wt.% of palladium was impregnated with an incipient-wetness method using an aqueous solution of Pd(NO₃)₂ (Aldrich, 38.7% Pd). Samples were dried at 100 °C overnight and calcined at 500 °C for 5 h under an atmosphere of air.

The activity of a commercial HDS catalyst (CoMo/Al₂O₃, Criterion Co.) was tested in comparison with the Pd-supported catalysts. Before use, the CoMo catalyst was ground (~100 μm) and pre-treated with a sulfidation–reduction under 5 vol.% H₂S/H₂ (50 ml/min) at 1 atm and 400 °C for 3 h. The pre-treated catalyst was denoted “CoMo-S”.

2.2. Characterization of catalysts

The specific surface area was determined via N₂ adsorption using a BET apparatus (ASAP 2010, Micrometrics). The samples were degassed at 300 °C under 4 mmHg overnight and the measurements were performed at 77 K.

The elemental compositions of the catalysts were measured by ICP-AES (Ultima 2C, Jobin Yvon) at the Korea Basic Science Institute (Seoul Branch). The results are presented in Table 1. The surface density of the tungsten, which refers to the number of tungsten atoms per specific surface area, is also listed in Table 1. The surface W density was calculated from Eq. (1), using BET and ICP-AES data.

$$\text{Surface density (SD, W/nm}^2\text{)} = \frac{\text{Concentration of W (g W/g cat.)} \times \text{Avogadro number (1/(mol W))}}{\text{BET area (m}^2\text{/g cat.)} \times \text{Atomic weight of W (g W/mol W)} \times 10^{18} \text{ (nm}^2\text{/m}^2\text{)}} \quad (1)$$

Raman spectroscopy (LabRam HR, Jobin-Yvon) was employed to identify the crystalline structure of the tungsten oxide on the WO₃/Al₂O₃ support. The measurements were performed at room temperature in the conventional back scattering geometry. The samples were excited with a 514.5 nm line of Ar-ion laser.

The acidic properties of the samples were examined using ammonia temperature programmed desorption (NH₃-TPD) and a pyridine adsorption method combined with FT-IR analysis, all of which were performed with the procedures described below.

For the NH₃-TPD analysis, the sample (0.15 g) was pre-treated at 500 °C for 1 h under a pure He flow (65 ml/min). The temperature was lowered to 110 °C before NH₃ was adsorbed on the sample under NH₃ gas (5 vol.% in He, 60 ml/min) for 1 h. The sample was flushed with flowing He (65 ml/min) at 110 °C for 1 h, and the NH₃ desorption was carried out under He flow (35 ml/min) while heating the sample from 110 to 650 °C at a rate of 10 °C/min. The temperature was maintained at 650 °C for 20 min to ensure the complete desorption of ammonia.

In the pyridine-adsorption experiments, thin pellet of 10 mm diameter was made by compressing the catalyst powders (ca. 13 mg) under 50 tons ram force. The pellet was mounted inside a specially designed Pyrex glass cell equipped with CaF₂ windows and heated at 280 °C for 1 h under a pure He stream (80 ml/min) followed by cooling to ambient temperature using the

same atmospheric conditions. Pyridine was adsorbed on the pellet by exposing it to pyridine vapor at ambient temperature. After adsorption, the pellet was subjected to a stream of pure helium for 10 min and were analyzed with IR spectroscopy (Nicolet 6700 FT-IR, Thermo Scientific). The IR spectra were recorded before and after the exposure to pyridine over a frequency range of 4000–400 cm⁻¹. The spectra were collected at a resolution of 4 cm⁻¹ using 32 scans per spectrum to improve the signal-to-noise ratio.

X-ray photoelectron spectroscopy (XPS) was performed using an ESCA2000 spectrometer (VG Microtech) under ultrahigh vacuum (10⁻⁹ torr). The powder sample was affixed on carbon tape and imaged using an Al Kα X-ray source (1486.6 eV). All the XPS signals were corrected using the C 1s reference at 284.6 eV.

The temperature-programmed reduction (H₂-TPR) was performed with the temperature increased from 50 to 300 °C (5 °C/min) under a 30 ml/min flow of 5 vol.% H₂/N₂ gas. Before measurement, the sample (0.05 g) was pre-treated by heating at 500 °C for 1 h under He flow (65 ml/min).

Hydrogen chemisorption was performed in a Micromeritics ASAP 2020 C apparatus. The sample was reduced under 2 MPa of hydrogen (99.999%) at 400 °C for 1 h. After reduction, the catalysts were degassed at 10⁻³ MPa for 10 h at 400 °C and cooled down to 70 °C with keeping evacuation for removing the physisorbed

hydrogen. Then, the H₂ chemisorption was performed at 70 °C and 0.007–0.08 MPa using the adsorption–backdesorption isotherm method. Through this, the formation of hydride (β-PdH phase) and spilt-over hydrogen could be avoided [51–53]. The amounts of chemisorbed hydrogen were calculated by extrapolation of the isotherms to zero pressure. Pd dispersion was calculated by assuming a stoichiometry H/Pd = 1 and spherical particles of palladium [51,54].

The X-ray diffraction (XRD) patterns were collected in a 2-theta range of 20–60° at a scanning rate of 2°/min on an X-ray powder diffractometer (DMAX-2500, Rigaku) using Cu Kα (λ = 1.5406 Å) irradiation.

2.3. HDO catalytic activity test

The reaction tests were performed in a 150 mL stainless steel autoclave batch reactor using 0.5 g of the catalyst at 300 °C under 7 MPa of hydrogen (>99.9%) and with an agitation rate of 300 rpm. Before reaction, the palladium catalysts were first charged in the reactor and reduced under 2 MPa of hydrogen at 400 °C for 1 h. The reactor was cooled down to room temperature and a reactant solution (50 ml) was charged to the reactor. The reactant fluid composed of 3 wt.% guaiacol (Sigma 0.21 mol/L) in *n*-decane (Sigma–Aldrich,

Table 2

Chemical composition and specific surface area of the PdSA and SA catalysts.

Nomenclature	Pd concentration ^a (wt.% Pd)	Si and Al concentration ^a		Si/Al atomic ratio	Specific surface area ^b (m ² g ⁻¹)
		(wt.% Si)	(wt.% Al)		
SA-0.6	–	37.3	62.7	0.57	512.3
SA-1.5	–	60.3	39.7	1.46	582.8
PdSA-1.9	2.03	66.2	33.8	1.88	505.2
SA-3.4	–	78.2	21.8	3.44	504.6
SA-6.4	–	87.0	13.0	6.44	486.9

^a Estimated from the Pd, Si and Al content obtained by ICP-AES.^b BET surface areas of the supports were analyzed by N₂ adsorption using ASAP2010.

≥99%). The reactor was purged several times with hydrogen to remove any remaining air. Eight samples were withdrawn 0, 15, 30, 45, 60, 90, 120 and 150 min after the reaction was initiated. The choice of these reaction conditions was based upon the blank test result performed without catalyst, which displayed negligible guaiacol conversion (2.2%).

In all of the tests, the gas phase was composed mainly of unreacted hydrogen and minor amounts of *n*-decane (less than 1 vol.%). Therefore, the analysis of product was achieved using the liquid phase. The liquid samples were analyzed with a gas chromatograph (6100GC, Young-Lin) equipped with a flame ionization detector (FID) and an HP-1 capillary column (30 m × 0.25 mm, film thickness of 1.0 μm).

The conversion of the guaiacol (X_{GUA} (%)) and the C₁-based yields of the products were calculated from Eqs. (2) and (3), respectively. In these equations, *n* presents the amount of the species in moles. The conversion and yield were determined by averaging three measured results.

$$X_{\text{GUA}} (\%) = \frac{n(\text{GUA})_{\text{initial}} - n(\text{GUA})_{\text{final}}}{n(\text{GUA})_{\text{initial}}} \times 100 \quad (2)$$

$$\text{C}_1\text{-based yield} (\%) = \frac{n(\text{prod.}) \times (\# \text{ of carbon of product compound})}{n(\text{GUA})_{\text{reacted}} \times (\# \text{ of carbon of GUA})} \quad (3)$$

3. Results and discussion

3.1. Characterization of catalysts

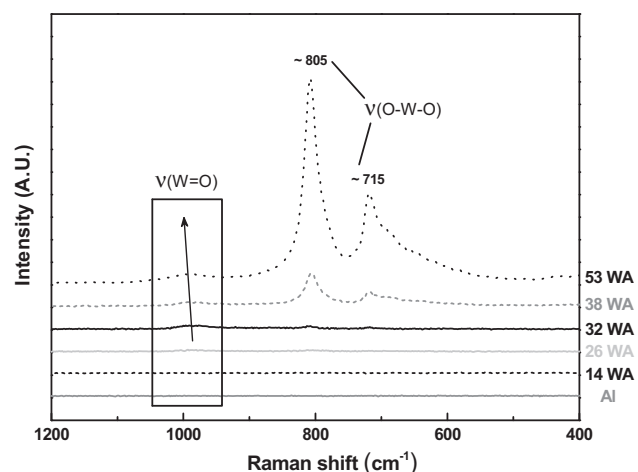
The elemental composition, specific surface area and surface W density of the Pd/WO_x/Al₂O₃ catalysts are presented in Table 1. The amounts of loaded Pd and W were close to the intended values. In Table 2, the elemental compositions and specific surface areas of the SiO₂–Al₂O₃ catalysts are also listed for later comparison with the Pd/WO_x/Al₂O₃ catalysts.

Raman spectroscopy was used to examine the molecular structure of WO_x on the WA supports (Fig. 1). The results of several studies indicated that the layered structure of WO_x was well correlated to the surface W density [37–40,55]. The Raman band at approximately 990–1000 cm⁻¹ represents the symmetric W=O stretching mode of the ‘dispersed’ tetrahedral-coordinated tungstate on alumina [55,56]. This peak was observed when more than 32 wt.% of W was loaded on the support and shifted from 990 to 995 cm⁻¹ as the W loading increased [55,56]. It was expected that the samples with lower W loading would also retain these tungstate species but, it was not observed due to the detection limit of the analysis. The Raman peaks at 715 and 805 cm⁻¹ appeared only for the samples containing more than 32 wt.% W (i.e., 38WA and 53WA). These peaks were assigned to the O–W–O vibrations of the ‘aggregated’ monoclinic WO₃ species [57,58]. It was known that when a monolayer of tungstate forms on the alumina, the

surface of the alumina is completely covered and there remains no externally exposed alumina surface [37,56]. The appearance of the ‘aggregated’ WO₃ species implied that the growth of the tungstate proceeded beyond the monolayer. Therefore, a tungstate monolayer without an aggregated phase would be formed in a WA material with a W loading between 26 and 32 wt.% or a surface W density between 3.7 and 5.0 W/nm². The result matched well with the work of Wachs’s group, who claimed that the monolayer coverage could be achieved at a surface W density of approximately 4.5 W/nm² [56]. Therefore, it was deemed that 32WA, which was free of aggregated bulk tungstate (on the Raman standard) and very near (5.0 W/nm²) to Wachs’s standard (~4.5 W/nm²) in surface W density, was almost completely (and solely) covered by the tungstate monolayer.

The amount of surface acid in the WA supports was estimated by NH₃-TPD analysis, and the results are presented in Fig. 2(a). The amount of acid (mmol NH₃/g) reached a maximum at 32WA, which featured a tungstate monolayer on its surface, and subsequently decreased as the W loading surpassed 32 wt.%. These results led us to conclude that the dispersed tungstate (in mono or sub-monolayer) was more acidic than the aggregated, bulk tungstate. When compared to the other acidic supports (SiO₂–Al₂O₃), 32WA was quite similar to SA-1.9 regarding TPD curve pattern (Fig. 2(b)), implying the two samples were almost equal in the amount of NH₃-desorption: 440 μmol NH₃/g (32WA) and 443 μmol NH₃/g (SA-1.9). Both catalysts will be compared with respect to catalytic activity in the next section.

The pyridine adsorption results (IR νCCN spectra) for the WA supports are provided in Fig. 3; these data were utilized to determine the concentrations of surface Lewis (L) and Brønsted (B) acid sites [59]. The peaks at approximately 1445 (L), 1490 (L+B) and 1540 (B) cm⁻¹ represent the Lewis and Brønsted acid sites [60]. The area of each peak was proportional to the concentration of the corresponding acid site. The concentrations of the Lewis and Brønsted

**Fig. 1.** Raman spectra of WA and Al supports relative to the W content (wt.% W).

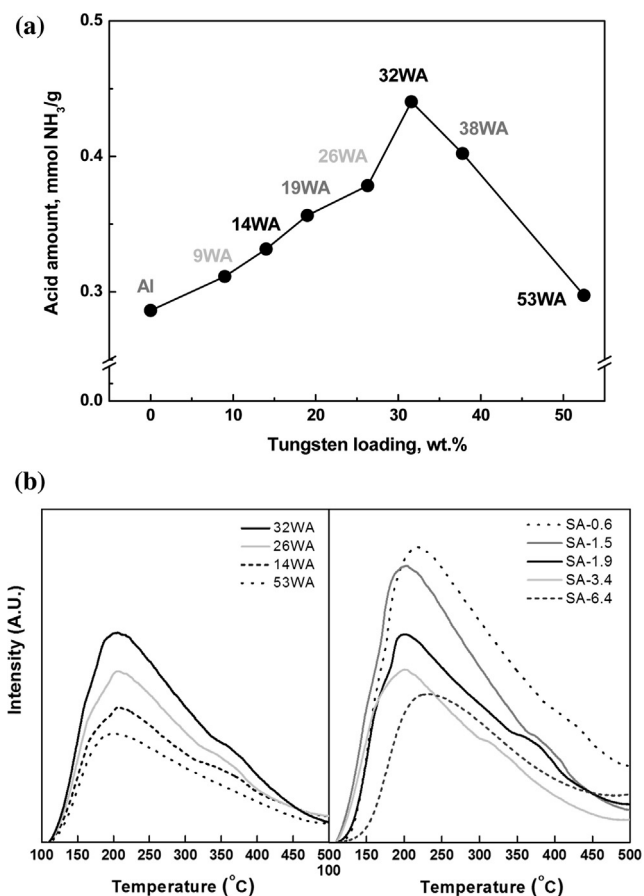


Fig. 2. (a) Amount of acid sites (mmol NH₃/g) on the WA and Al supports and (b) NH₃-TPD patterns of the WA and Si/Al supports.

acid sites peaked at 32WA and subsequently began to decrease when the W loading increased past 32 wt.%, which validated the previously explained NH₃-TPD result (Fig. 2).

Fig. 4 presents Pd 3d and W 4f XPS spectra of the catalysts before and after reduction, which were compared to the data

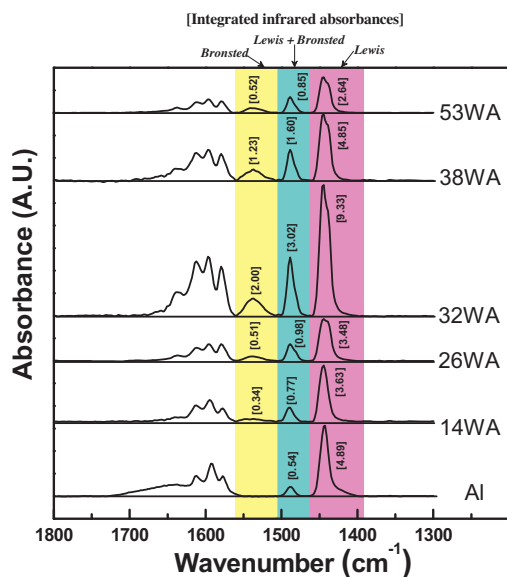


Fig. 3. IR νCCN spectra of irreversibly adsorbed pyridine at ambient temperature. The values in the brackets are the integrated infrared absorbances.

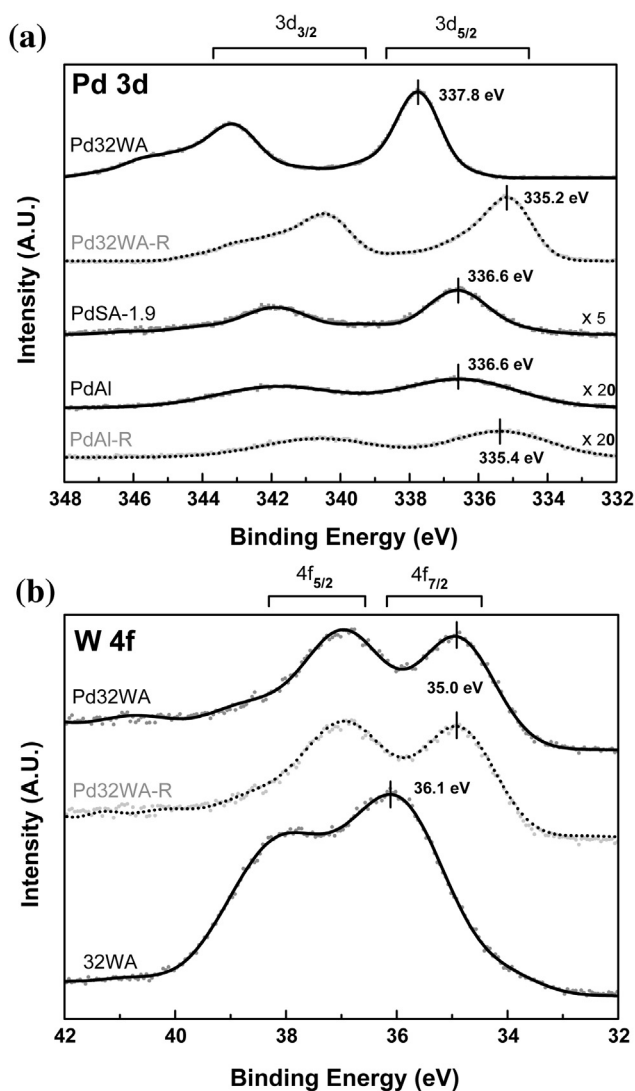


Fig. 4. XPS spectra of (a) Pd 3d in PdAl and Pd32WA and (b) W 4f in 32WA and Pd32WA.

from other supported catalysts. The *ex situ* reduction of catalysts was performed at 400 °C for 1 h with H₂ gas in the reactor. The spectra of the reduced catalysts were marked with the suffix “-R” in Fig. 4. The Pd 3d_{5/2} binding energy of Pd32WA (not reduced) was observed at 337.8 eV, which could be assigned to Pd⁴⁺ (PdO₂), whereas the corresponding value for the other Pd catalysts (PdAl, PdSA-1.9) appeared at 336.6 eV, which was close to the binding energy of Pd²⁺ (PdO) [61,62] (Fig. 4(a)). PdO₂ is an unstable oxide which is known to degrade, forming PdO above 200 °C [61,63]. Otto et al. reported that PdO₂ could be stabilized in Pd/Al₂O₃ if the Pd was highly dispersed and present in amounts less than 0.5 wt.% over alumina [61]. Therefore, the palladium and alumina must interact with each other properly to successfully stabilize PdO₂ on the alumina surface. PdO was found instead of PdO₂ in our Pd/Al₂O₃ (not reduced) catalyst (PdAl in Fig. 4(a)) because the Pd loading was comparatively high (2 wt.%), which matched well with the Otto group's result. On the contrary, PdO₂ was the dominant species in Pd32WA (not reduced) even though the Pd loading was almost same (2 wt.%). Additionally, Pd32WA was higher than other Pd catalysts in the intensity of Pd 3d XPS peak, that is, the highest in Pd dispersion. Therefore, we could assume that the palladium interacted closely with the tungstate monolayer in Pd32WA based on these results. Meanwhile, Fig. 4(b) indicates that the W 4f_{7/2}

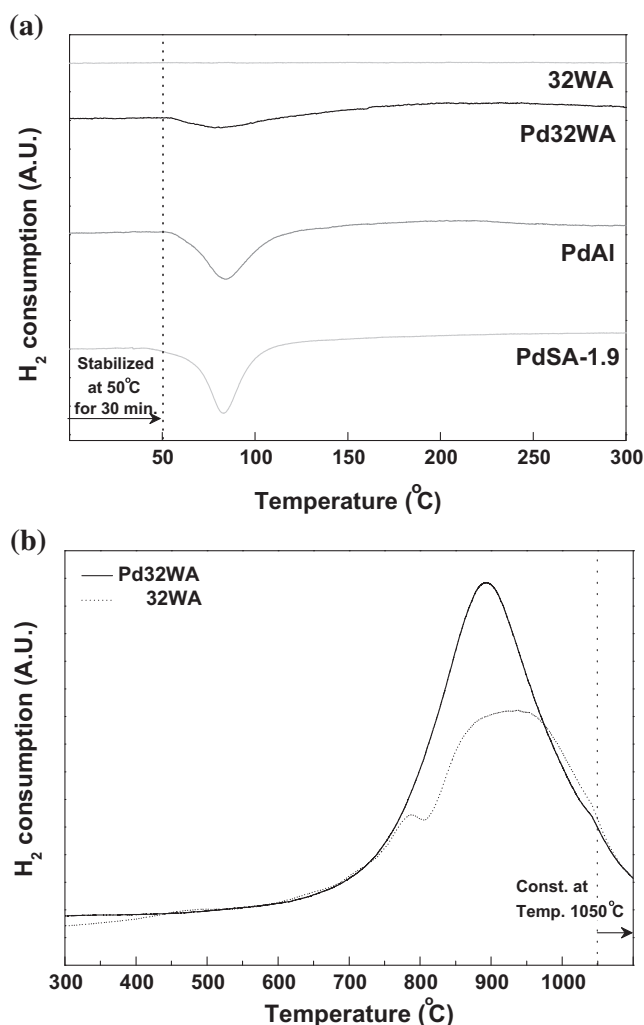


Fig. 5. TPR results (a) at a low temperature range (<300 °C) and (b) at a high temperature range (>500 °C).

peak was shifted from 36.1 (32WA) to 35 eV (Pd32WA) as Pd was loaded onto the WA support. It was expected to result from the interaction between Pd and WO_x , which causes the tungsten to become relatively electron-rich (to be more exact, less electron-deficient) via electron donation from palladium [48,49]. With *ex situ* reduction, the Pd $3d_{5/2}$ binding energies of the Pd32WA and PdAl were shifted to lower energies, 335.2 and 335.4 eV, respectively (see the data for Pd32WA-R and PdAl-R in Fig. 4(a)), both of which were assigned to Pd^0 (metallic Pd) [64,65]. The XPS intensities of both catalysts were not changed after reduction. On the other hand, W $4f_{7/2}$ spectra of Pd32WA and Pd32WA-R were nearly identical to each other, which imply that the tungsten oxide layer is not reduced under the reduction (or reaction) condition.

The TPR results are provided in Fig. 5. The negative peaks appearing at ~ 80 °C for the Pd catalysts (Fig. 5(a)) were assigned to the desorption of the hydrogen weakly adsorbed on palladium, as well as the decomposition of the palladium hydride (*beta*-PdH) formed on the metallic palladium at ambient temperatures [48,66,67]. The negative peak for Pd32WA was smaller than for the other Pd catalysts: It could be explained by a partial decoration of the perimeter of the Pd particles by a WO_x overlayer in Pd32WA [48], which was induced as a result of close interaction between Pd and WO_x . In this case, the Pd– WO_x interaction would reduce the exposed palladium surface area, which causes a decrease in the Pd sites accessible for hydrogen adsorption (this hypothesis will be confirmed when the

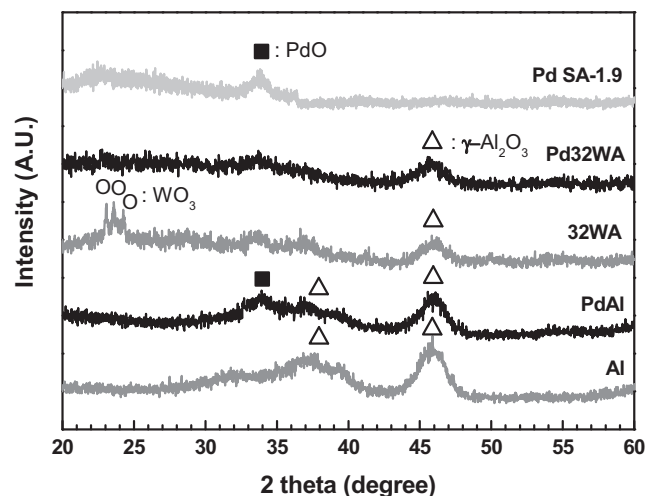


Fig. 6. XRD patterns of Al, PdAl, 32WA, Pd32WA and PdSA-1.9.

H_2 chemisorption results are explained). On the other hand, this partial decoration improved the physical contact between Pd and WO_x and therefore enhanced the reduction of the tungstate during the high-temperature run of TPR experiments (over 700 °C): Fig. 5(b) clearly demonstrates that the rate of high-temperature reduction (over 700 °C) for Pd32WA was much faster than for WA.

Table 3 summarizes the H_2 chemisorption results. The results contradicted the Pd 3d XPS data (Fig. 3(a)): Pd32WA was smaller than PdAl in Pd dispersion, which was the opposite of the XPS results. This observation could be explained by the decrease in the Pd surface site accessible to hydrogen, which was caused by the WO_x overlayer. In the XPS analysis, it was expected that, because X-ray possibly penetrated the WO_x overlayer, the photoelectrons from the ‘over-layered’ Pd surface region could be counted as well.

Fig. 6 presents the XRD patterns for the catalysts. For the γ -alumina supported catalysts (PdAl, 32WA and Pd32WA), the XRD patterns contained the lines typical of γ - Al_2O_3 framework ($2\theta = 38.0, 46.0$ from JCPDS 10-0425), implying that the alumina retained its structure after the W and Pd were added. The intensity of the alumina signals decreased slightly as the tungsten was loaded. The tungsten oxide peaks of 32WA appeared at $2\theta = 23.3^\circ, 23.8^\circ$, and 26.6° , which were attributed to the aggregated monoclinic tungstate phase *slightly* exceeding the monolayer coverage (JCPDS 20-1324) [68]. However, those tungstate peaks disappeared on the XRD spectrum of Pd32WA.

3.2. Catalytic activity

In Fig. 7, the HDO activities of the Pd/ WO_x / Al_2O_3 catalysts are presented as a function of W loading and compared with the activities of the other catalysts.

In almost every case, more than 30 products were detected during GC–MS analysis. Of the products, we evaluated yields for the species accounting for more than 1% (v/v) of the sample (with excluding volume of solvent in a sample). Therefore, the targets for analysis were catechol (benzene-1,2-diol), phenol (hydroxyl-benzene), cresol (methyl-phenol), anisole (methoxybenzene) and cyclohexane. The other minor products were treated as a combination labeled “Others” when calculating yields and included toluene, benzene, 1,3,5-trimethyl-benzene, 3,5-dimethyl-phenol, 3-methyl-1,2-benzenediol, 2-methoxy-5-methyl-phenol, 2,4,5-trimethyl-phenol, 3,4,5-trimethylphenol, 2,4,6-trimethylphenol, 4,5-dimethyl-2,3-benzenediol, and 2,5-dimethyl-hydroquinone, etc. Because the yields were obtained by means of C_1 -based calculation, the summation of the product yields (i.e., the total height

Table 3

Chemisorption results for the PdAl, PdSA-1.9 and Pd32WA catalysts.

Catalysts	Pd dispersion (%)	Pd surface area ($\text{m}^2 \text{g}_{\text{metal}}^{-1}$)	Pd crystallite size (nm)	Hydrogen adsorbed ($\mu\text{mol H}_2/\text{g}_{\text{cat.}}$)
PdAl	20.8	92.8	5.4	58
Pd32WA	0.2	0.7	n.d.	7
PdSA-1.9	2.9	13.1	38.1	56

n.d.: not determined.

of a bar in Fig. 7) was equal to the guaiacol conversion. The minor products were classified as “Others” in the figure. There were differences in the content of minor products among the catalysts, so each “Others” bar was shaded differently. The guaiacol conversion and product yields in Fig. 7 were calculated from the reaction results obtained 150 min after the reaction began. The reactions had usually reached a steady state at this point, which is confirmed in Fig. 8.

Fig. 7 indicates that the conversion of guaiacol reached 100% for all the palladium catalysts and produced predominantly cyclohexane, which is the final product in a forward-driven HDO of guaiacol (Scheme 1). For the PdWA catalysts, the yield of cyclohexane reached the maximum (88.4%) when the W loading was 32 wt.% (i.e., Pd32WA). Compared to Pd32WA, PdSA-1.9 contained almost an equal amount of Pd (2 wt.%) and also contained a similar amount (and distribution) of total acid in the support materials (as examined in NH_3 -TPD analysis, Fig. 2). However, the yield of cyclohexane with PdSA-1.9 was much lower (50.8%) than the yield with Pd32WA. As shown previously in the XPS results (Fig. 4(a)), there was a noticeable difference between Pd32WA and PdSA-1.9 with regard to the physicochemical state of palladium. If we assumed the catalysts work on the *bi-functional* reaction mechanism (Scheme 1 (b)), specifically hydrogenation (by Pd) and deoxygenation (by acid sites), the differences in the state of the Pd would influence the cyclohexane yield more decisively because the acidic properties of 32WA and SA-1.9 were similar. The support materials (32WA and SA-1.9, without palladium) were tested for HDO activity and compared to each other (Fig. 7). With only the support materials, the guaiacol conversions were relatively low and catechol was obtained as the major product, implying that the reaction rate was retarded in absence of Pd. Based on the acid-driven reaction mechanism suggested in Scheme 1(a), it was expected that the reaction had not progressed sufficiently and remained in the stage of catechol.

For the sulfided HDS commercial catalysts (CoMo-S), the guaiacol conversion was 95%, but the majorly obtained products were different from those of the Pd catalysts. The formation of catechol and phenol was observed, implying that the demethylation

or deoxygenation of guaiacol occurred on this catalyst. The methylated compound, such as cresol (methyl-phenol), was also observed, implying that the methyl group (cleaved from guaiacol) was attached to the phenol formed during the reaction [8].

Explained in ‘introduction,’ noble metal-supported acidic oxide catalysts reportedly follow a hydrogenation–deoxygenation, *bifunctional* mechanism (Scheme 1(b)) [22]. As we have assumed beforehand, the same mechanism might be applied to the HDO of guaiacol over the Pd32WA catalyst, which was confirmed by the reactions carried out at low temperatures (220 and 250 °C). At these temperatures, the rates of the constituent reactions would be slower than are exhibited at 300 °C, increasing the probability of detecting the intermediate species (i.e., 2-methoxycyclohexanol, cyclohexanol, etc.). The time-stream measurements of guaiacol conversion and product yields were made at 200, 250 and 300 °C, and the results are compared in Fig. 8. 2-Methoxycyclohexanol, which was produced via *full* hydrogenation of guaiacol's aromatic ring, was observed in the 200 °C reaction. When the temperature was raised to 250 °C, the formation of cyclohexanol was observed; this product would be formed via the demethoxylation of the first intermediate, 2-methoxycyclohexanol. Clearly, the reaction proceeded further (through dehydroxylation of cyclohexanol) toward cyclohexane at and above 250 °C. Therefore, it was confirmed that the HDO reaction on Pd32WA followed the *bi-functional* reaction pathway known for noble-supported acidic oxide catalysts, which is suggested in Scheme 1(b).

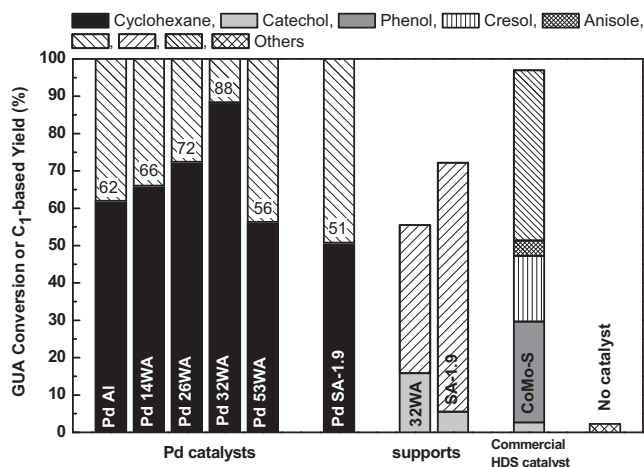


Fig. 7. Conversion of guaiacol (GUA) and C_1 -based yields of the products over various catalysts at 300 °C, 300 rpm, 7 MPa of H_2 and 150 min.

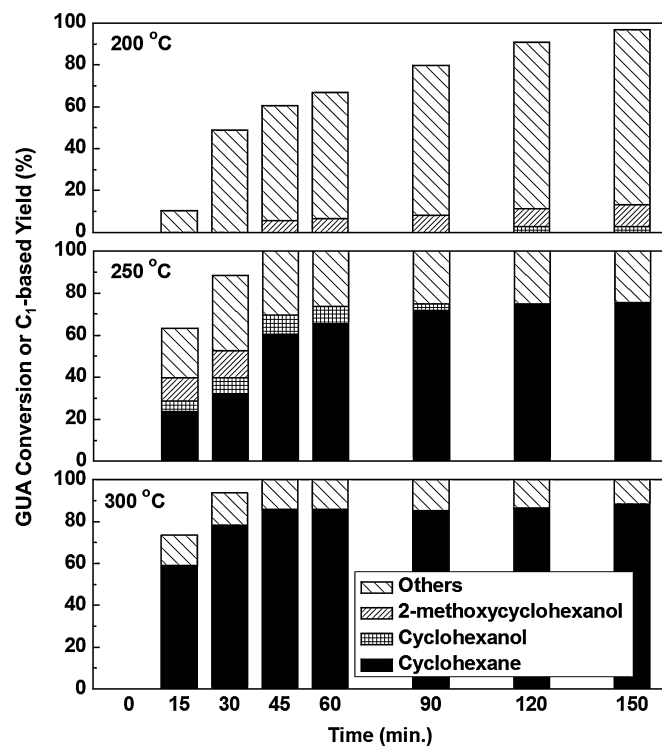


Fig. 8. Conversion of guaiacol (GUA) and C_1 -based yields of products over Pd32WA as a function of time at different temperatures (200, 250, 300 °C). The conditions were same as those listed in Fig. 7.

4. Conclusion

Guaiacol was hydrodeoxygenated on Pd/WO_x/Al₂O₃ (PdWA) catalyst via the stepwise, bi-functional mechanism: (1) the full hydrogenation of the aromatic ring (by Pd); (2) the deoxygenation of methoxy and hydroxyl groups (by Pd-acid sites). Therefore, the HDO activity of Pd32WA was related to the acidic strength of the WA support and the physicochemical state of palladium.

The tungsten loading directly affected the HDO activity, which was related to the surface acidity of the catalyst. The highest HDO activity was achieved with 32 wt.% W loading (Pd32WA). This result is attributed to the formation of a tungstate monolayer over the alumina support, making 32WA the most acidic of the prepared WA supports.

The Pd species on Pd32WA interacted closely with the support (32WA): in the XPS results, the electronic interaction was observed via the electron transfers from Pd to W. The morphological effect of the metal–support interaction was also observed via the decoration of perimeter of palladium by tungstate overlayer, which hindered the H₂ chemisorption by limiting the access of hydrogen to palladium surface.

Pd32WA demonstrated the highest yield (88%) of cyclohexane of the Pd/WO_x/Al₂O₃ catalysts tested. Pd32WA displayed higher activity than PdSA-1.9, which was similar in terms of Pd loading and amount of acidic surface sites, implying that the Pd species interacting with the WO_x/Al₂O₃ support were especially effective at promoting HDO of guaiacol.

Acknowledgements

This work was supported by the MSIP (Ministry of Science, ICT & Future Planning) of Korea Grant funded by the Korean Government (NRF-2012R1A2A1A03009667).

Dr. Dae-Won Lee was personally supported by Korea University Grant.

References

- [1] J.G. Speight, *Heavy and Extra-heavy Oil Upgrading Technologies*, Gulf Professional Publishing, Boston, 2013, pp. 1–13.
- [2] A. Demirbas, *Energy Conversion and Management* 42 (2001) 1357–1378.
- [3] J.v. Haveren, E.L. Scott, J. Sanders, *Biofuels, Bioproducts and Biorefining* 2 (2008) 41–57.
- [4] J. Chattopadhyay, J. Son, D. Pak, *Korean Journal of Chemical Engineering* 28 (2011) 1677–1683.
- [5] M. Ferrari, B. Delmon, P. Grange, *Carbon* 40 (2002) 497–511.
- [6] A. Gutierrez, R.K. Kaila, M.L. Honkela, R. Slioor, A.O.I. Krause, *Catalysis Today* 147 (2009) 239–246.
- [7] D. Mohan, C.U. Pittman, P.H. Steele, *Energy & Fuels* 20 (2006) 848–889.
- [8] V.N. Bui, G. Toussaint, D. Laurenti, C. Mirodatos, C. Geantet, *Catalysis Today* 143 (2009) 172–178.
- [9] A. Centeno, E. Laurent, B. Delmon, *Journal of Catalysis* 154 (1995) 288–298.
- [10] M. Ferrari, S. Bosmans, R. Maggi, B. Delmon, P. Grange, *Catalysis Today* 65 (2001) 257–264.
- [11] M. Ferrari, R. Maggi, B. Delmon, P. Grange, *Journal of Catalysis* 198 (2001) 47–55.
- [12] E. Laurent, B. Delmon, *Applied Catalysis A: General* 109 (1994) 77–96.
- [13] E. Laurent, B. Delmon, *Applied Catalysis A: General* 109 (1994) 97–115.
- [14] E. Laurent, B. Delmon, *Journal of Catalysis* 146 (1994) 281–291.
- [15] M.V. Bykova, D.Y. Ermakov, V.V. Kaichev, O.A. Bulavchenko, A.A. Saraev, M.Y. Lebedev, V.A. Yakovlev, *Applied Catalysis B: Environmental* 113–114 (2012) 296–307.
- [16] R.N. Olcese, M. Bettahar, D. Petitjean, B. Malaman, F. Giovannella, A. Dufour, *Applied Catalysis B: Environmental* 115–116 (2012) 63–73.
- [17] R. Olcese, M.M. Bettahar, B. Malaman, J. Ghanbaja, L. Tibavizco, D. Petitjean, A. Dufour, *Applied Catalysis B: Environmental* 129 (2013) 528–538.
- [18] Y. Romero, F. Richard, S. Brunet, *Applied Catalysis B: Environmental* 98 (2010) 213–223.
- [19] V.N. Bui, D. Laurenti, P. Afanasiev, C. Geantet, *Applied Catalysis B: Environmental* 101 (2011) 239–245.
- [20] V.N. Bui, D. Laurenti, P. Delichère, C. Geantet, *Applied Catalysis B: Environmental* 101 (2011) 246–255.
- [21] R. Nava, B. Pawelec, P. Castañó, M.C. Álvarez-Galván, C.V. Loricera, J.L.G. Fierro, *Applied Catalysis B: Environmental* 92 (2009) 154–167.
- [22] C.R. Lee, J.S. Yoon, Y.-W. Suh, J.-W. Choi, J.-M. Ha, D.J. Suh, Y.-K. Park, *Catalysis Communications* 17 (2012) 54–58.
- [23] Y.-C. Lin, C.-L. Li, H.-P. Wan, H.-T. Lee, C.-F. Liu, *Energy & Fuels* 25 (2011) 890–896.
- [24] C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, *Angewandte Chemie International Edition* 48 (2009) 3987–3990.
- [25] A.V. Bridgewater, *Applied Catalysis A: General* 116 (1994) 5–47.
- [26] G. Chahboun, C.E. Petrisor, E. Gomez-Bengoa, E. Royo, T. Cuenca, *European Journal of Inorganic Chemistry* 2009 (2009) 1514–1520.
- [27] P. Lukinskas, S. Kuba, R.K. Grasselli, H. Knoezinger, *Topics in Catalysis* 46 (2007) 87–92.
- [28] S. Djerad, L. Tifouti, M. Crocoll, W. Weisweiler, *Journal of Molecular Catalysis A: Chemical* 208 (2004) 257–265.
- [29] B.W. Lee, H. Cho, D.W. Shin, *Journal of Ceramic Processing Research* 8 (2007) 203–207.
- [30] E. Rodriguez-Castellon, A. Jimenez-Lopez, D. Eliche-Quesada, *Fuel* 87 (2008) 1195–1206.
- [31] R. Huirache-Acuna, F. Paraguay-Delgado, M.A. Albiter, L. Alvarez-Contreras, E.M. Rivera-Munoz, G. Alonso-Nunez, *Journal of Materials Science* 44 (2009) 4360–4369.
- [32] A.J. Duan, R.L. Li, G.Y. Jiang, J.S. Gao, Z. Zhao, G.F. Wan, D.Q. Zhang, W.Q. Huang, K.H. Chung, *Catalysis Today* 140 (2009) 187–191.
- [33] S.L. Soled, G.B. McVicker, L.L. Murrell, L.G. Sherman, N.C. Dispenziere, S.L. Hsu, D. Waldman, *Journal of Catalysis* 111 (1988) 286–295.
- [34] J. Macht, C.D. Baertsch, M. May-Lozano, S.L. Soled, Y. Wang, E. Iglesia, *Journal of Catalysis* 227 (2004) 479–491.
- [35] R. Zhang, J. Jagiello, J.F. Hu, Z.Q. Huang, J.A. Schwarz, A. Datye, *Applied Catalysis A: General* 84 (1992) 123–139.
- [36] I. Rodríguez-Ramos, A. Guerrero-Ruiz, N. Homs, P.R. de la Piscina, J.L.G. Fierro, *Journal of Molecular Catalysis A: Chemical* 95 (1995) 147–154.
- [37] S.S. Chan, I.E. Wachs, L.L. Murrell, N.C. Dispenziere, *Journal of Catalysis* 92 (1985) 1–10.
- [38] J.A. Horsley, I.E. Wachs, J.M. Brown, G.H. Via, F.D. Hardcastle, *Journal of Physical Chemistry* 91 (1987) 4014–4020.
- [39] M.A. Vuurman, I.E. Wachs, *Journal of Physical Chemistry* 96 (1992) 5008–5016.
- [40] I.E. Wachs, *Catalysis Today* 27 (1996) 437–455.
- [41] Y. Li, Y. Fan, H. Yang, B. Xu, L. Feng, M. Yang, Y. Chen, *Chemical Physics Letters* 372 (2003) 160–165.
- [42] J. Hong, W. Chu, M. Chen, X. Wang, T. Zhang, *Catalysis Communications* 8 (2007) 593–597.
- [43] Y. Li, B. Xu, Y. Fan, N. Feng, A. Qiu, J.M.J. He, H. Yang, Y. Chen, *Journal of Molecular Catalysis A: Chemical* 216 (2004) 107–114.
- [44] M. Koussathana, N. Vamvouka, M. Tsapatsis, X. Verykios, *Applied Catalysis A: General* 80 (1992) 99–113.
- [45] A. Binder, M. Seipenbusch, M. Muhler, G. Kasper, *Journal of Catalysis* 268 (2009) 150–155.
- [46] A.M. Sica, I.M. Baibich, C.E. Gigola, *Journal of Molecular Catalysis A: Chemical* 195 (2003) 225–233.
- [47] J. Plšek, I. Jirka, V. Nikolajenko, Z. Knor, *Surface Science* 600 (2006) 3943–3949.
- [48] C.R. Lederhos, M.J. Maccarrone, J.M. Badano, G. Torres, F. Coloma-Pascual, J.C. Yori, M.E. Quiroga, *Applied Catalysis A: General* 396 (2011) 170–176.
- [49] P.C. L'Argentier, N.S. Figoli, *Industrial & Engineering Chemistry Research* 36 (1997) 2543–2546.
- [50] J. Lee, S. Hwang, J.G. Seo, U.G. Hong, J.C. Jung, I.K. Song, *Journal of Industrial and Engineering Chemistry* 17 (2011) 310–315.
- [51] J.E. Benson, H.S. Hwang, M. Boudart, *Journal of Catalysis* 30 (1973) 146–153.
- [52] V. Ragaini, R. Giannantonio, P. Magni, L. Lucarelli, G. Leofanti, *Journal of Catalysis* 146 (1994) 116–125.
- [53] C.I. Contescu, C.M. Brown, Y. Liu, V.V. Bhat, N.C. Gallego, *Journal of Physical Chemistry C* 113 (2009) 5886–5890.
- [54] I. Kirm, F. Medina, X. Rodríguez, Y. Cesteros, P. Salagre, J.E. Sueiras, *Journal of Molecular Catalysis A: Chemical* 239 (2005) 215–221.
- [55] D.S. Kim, M. Ostromecki, I.E. Wachs, *Journal of Molecular Catalysis A: Chemical* 106 (1996) 93–102.
- [56] I.E. Wachs, T. Kim, E.I. Ross, *Catalysis Today* 116 (2006) 162–168.
- [57] M.F. Daniel, B. Desbat, J.C. Lassegues, B. Gerand, M. Figlarz, *Journal of Solid State Chemistry* 67 (1987) 235–247.
- [58] B. Ingham, S.V. Chong, J.L. Tallon, *Journal of Physical Chemistry B* 109 (2005) 4936–4940.
- [59] Israel E. Wachs, *Catalysis Today* 27 (1996) 437–455.
- [60] B.T. Loveless, A. Gyanani, D.S. Muggli, *Applied Catalysis B: Environmental* 84 (2008) 591–597.
- [61] K. Otto, L.P. Haack, J.E. de Vries, *Applied Catalysis B: Environmental* 1 (1992) 1–12.
- [62] M. Moroseac, T. Skála, K. Veltruská, V. Matolín, I. Matolínová, *Surface Science* 566–568 (Part 2) (2004) 1118–1123.
- [63] J.G. McCarty, *Catalysis Today* 26 (1995) 283–293.
- [64] A.I. Boronin, E.M. Slavinskaya, I.G. Danilova, R.V. Gulyaev, Y.I. Amosov, P.A. Kuznetsov, I.A. Polukhina, S.V. Koscheev, V.I. Zaikovskii, A.S. Noskov, *Catalysis Today* 144 (2009) 201–211.
- [65] S.-H. Oh, G.B. Hoflund, *Journal of Physical Chemistry A* 110 (2006) 7609–7613.
- [66] C.-B. Wang, H.-K. Lin, C.-M. Ho, *Journal of Molecular Catalysis A: Chemical* 180 (2002) 285–291.
- [67] V.V. Alegre, M.A.P. da Silva, M. Schmal, *Catalysis Communications* 7 (2006) 314–322.
- [68] G. Xin, W. Guo, T. Ma, *Applied Surface Science* 256 (2009) 165–169.